DETERMINATION OF VOLUME SOLIDS OF PAINTS AND COATINGS BY ACCURATE DRY FILM THICKNESS MEASUREMENTS

MARCH, 1981

Prepared by:

Georgia Institute of Technology
Engineering Experiment Station
in cooperation with
Avondale Shipyards, Inc.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
MAR 1981	**N/A**	**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Determination of Volume Solids of Paints and Coatings by Accurate Dry Film Thickness Measurements	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Surface Warfare Center CD Code 2230 - Design Integration Tools Building 192 Room 128 9500 MacArthur Bldg Bethesda, MD 20817-5700**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**SAR**	**41**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

FOREWORD

Avondale Shipyards, Inc. has been contracted by the U.S. Department of Commerce, Contract No. 5-38071, to manage its research and development efforts in the area of surface preparation and coating.

Pursuant with this responsibility, the following research and development was sub-contracted to the Engineering Experiment Station, Georaia Institute of Technology.

"Development of a Standard Procedure for Determining Volume Solids of Coatings."

This research project was undertaken with the primary objective as the development of a standard analytical procedure to determine the volume solids of liquid coatings. The volume solids obtained was to accurately represent the volume of dried coating film (coverage) obtained from a gallon of liquid material.

Successful completion of the work would, at least, provide a detailed procedure for measuring the volume solids of coatings used in the marine industry. Once these procedures are adopted by the marine industry, coating suppliers can be required to report the volume solids on that basis and not values calculated from a formula sheet. This would help in estimating the quantity of paint required for various jobs, minimizing the probability of purchasing too little or too much paint with obvious dollar savings. With better volume solids data, the estimate of painting time can also be made more accurately using, for example, the effective solids output parameter promoted by Ginsberg.[1]

Mr. Leslie E. Henton, of the Engineering Experiment Station, served as Principal Investigator. Mr. Wayne Case, of the same institute, performed

all testing operations. On behalf of Avondale Shipyards, Inc., Mr. John Peart was the R & D Project Manager responsible for technical direction, editing, and publication of this report.

Special thanks are given to Mr. David Hurst, of the Engineering Experiment Station, Georgia Institute of Technology, for the film thickness measurement concept and to Mr. W. R. Tooke, Jr. of Micro-Metrics Company for supplying data from an ASTM round robin on dry film measurements. Also, we wish to acknowledge the contributions of the following corporations:

Avondale shipyards, Inc., New Orleans, Louisiana

Carboline Marine Corporation, St. Louis, Missouri

Farboil Company, Baltimore, Maryland

General Polymers Corporation, Cincinnati, Ohio

Imperial Coatings Corporation, New Orleans, Louisiana

International Paint Company, Inc., Union, New Jersey

Jotun-Baltimore Copper Paint Company, Baltimore, Maryland

Matcote Company, Inc., Houston, Texas

NAPCO Corporation, Houston, Texas

Porter Coatings, Louisville, Kentucky

Sigma Coatings, Harvey, Louisiana

EXECUTIVE SUMMARY

A new method to determine the volume solids of paints and coatings based on the measurement of dried film thickness over a known area has been studied in this work. It was compared to the American Society for Testing and Materials Method D 2697-73 Volume Nonvolatile Matter in Clear and Pigmented Coatings. This method determines the volume of the dry film by application of the Archimedes buoyancy effect. In addition, the project was structured to extend the ASTM method to coatings systems used in the marine industry.

The volume solids of several typical marine coating systems were determined using the proposed film thickness method as well as the current ASTM method. The type of coatings examined were ketimine cured epoxies, amine and amine adduct cured epoxies, polyamide cured epoxies, vinlys, chlorinated rubbers, alkyds, inorganic zinc-rich coatings, urethanes, and waterborne coatings. The film drying or curing conditions used were appropriate to the chemistry involved in the film forming process.

The results indicate that the precision of the ASTM method is better than the precision of the film thickness method. This is primarily due to poor film thickness uniformity. It was also shown that there is no benefit in time savings and sample handling in making volume solids determinations by the film thickness technique, when the manufacturer's recommended conditioning schedule is used to cure the paint film. The ASTM Method, then is the preferred one.

From the results of the work on this project, it is concluded that the user and the paint supplier must agree upon the curing or conditioning schedule, as the curing conditions can affect the volume solids values obtained.

Any further work done in pursuing the film thickness technique should be in the direction of obtaining a method that will give samples with uniform film thickness.

SECTION 1
Conclusions

CONCLUSIONS

1. The precision in the film thickness method is much less than the precision of the ASTM method. This is due to the lack of film thickness uniformity.
2. There is no benefit in time savings and sample handling in making a volume solids determination by the film thickness method in comparison with the ASTM method.
3. The curing conditions can affect the volume solids values obtained so it is imperative that the manufacturer and user agree upon the conditioning schedule. This is already recognized in the ASTM method.
4. Although there were cases where the volume solids values obtained by the two methods agreed in terms of the student’s t-test, the large variances in the film thickness method may negate the validity of those agreements.

SECTION 2

Project Plan of Action and Results

2. PROJECT PLAN OF ACTICN AND RESULTS

2.1 Objective

The objective was development of a standard analytical procedure for determining the volume solids of liquid coatings. The volume solids obtained was to accurately represent the volume of dried coating film (coverage) obtained from a gallon of liquid material.

2.2 General Approach

The present ASTM method for the determination of the volume solids of clear and pigmented coatings, ASTM D 2697-73,[2] is based on the indirect measurement of the volume of a dried paint film using the Archimedes buoyancy effect. The weight of the paint film, supported on a metal substrate, is determined in air and in some liquid of known specific gravity. The weight (mass) difference divided by the specific gravity of the liquid gives the volume of the paint film. This data in combination with the weight solids and the specific gravity of the wet paint is then used to calculate the volume solids. In principal, this method is highly accurate since it is based on well established gravimetric techniques. The method, however, is not used widely in the coatings industry. Volume solids typically are calculated from formulations or batch sheets using the density of the individual components and assuming that the volumes are additive. This assumption is, in general, incorrect. Hence, experimental volume solids and calculated volume solids will be different; the maqnitude of this difference will be dependent on the magnitude of the error in assuming that the volumes are additive.

There are sources for error or differing interpretations to the application of ASTM D 2697-73 to the wide range of paints and coatings found In industry. One must determine if, for example, voids or pores

are a proper part of the final film structure for, if so, a liquid must be used that will not penetrate into these voids. The displacement liquids used must also not be absorbed into the paint film, at least in the time it takes to make the weight measurements. Reasonable, intelligent modifications to the method must also be made based on the chemistry involved in the film forming process for each coating tested. Here, a particularly sensitive point is the conditioning procedures for obtaining a final dried film and the determination of the weight non-volatiles of the coating. The current method recommends drying for three hours at 105°C although this is qualified by a note which identifies the best drying conditions as those recommended by the manufacturer of the coating and similar to the in-use curing conditions. Unintentional abuses of the drying procedure have occurred. For example, a coating based on unsaturated polyester cured or crosslinked by in-situ, room temperature polymerization with styrene was subjected to the 105°C heating.[3] This, of course, volatilized the styrene, a normal component of the dried coating, which lead to completely erroneous results. Similar problems can be expected in systems that use low molecular weight matrials that are crosslinked into the final film by reaction with absorbed water vapor such as urethane systems or ketimine-epoxy systems. It seems obvious, at this point that for the wide range of coatings used in the marine industry appropriate methods of film drying or curing for volume solids measurements must be examined and developed

2.2.1.News, Proposed Methods

A method to determine the volume solids of paints and coatings based on the measurement of dried film thickness has been studied in this work. The method does not require the selection of a displacement liquid so that errors due to the penetration or non-penetration of the liquid into pores and/or voids and the swelling/absorption properties of the coating-liquid

system are avoided.

The new method entails the measurement of the weight of the wet, freshly applied coating, the specific gravity of the wet coating, and its dry film thickness over a known area. Drying or curing conditions are selected appropriate to the coating system.

The volume solids, $, of a paint or coating in this alternate method is given by

$$\phi = A \tau \rho / W \tag{1}$$

where A is the area of the film, τ is its thickness, ρ is the density of the wet paint, and W is the weight of the wet coating applied to area A. That is, the initial volume of paint applied is

$$V_i = W/\rho \tag{2}$$

and the final volume is

$$V_f = A_T \tag{3}$$

In any experimental determination of a quantity, there are errors in the measurements which introduce uncertainties into the final, calculated value. The error analysis of the film thickness measurement technique performed here is based on a standard propagation of errors approach.[4] It represents the largest error in the volume solids one can reasonably expect.

The limit of error in the volume solids, $\lambda(\phi)$ is given by

$$\lambda(\phi) = \frac{A\tau}{W}\ \lambda(\rho) + \frac{A\rho\lambda(\tau)}{W} + \frac{\tau\rho}{W}\ \lambda(A) + \frac{A\tau\rho}{W^2}\ \lambda(W) \qquad (4)$$

where $\lambda(\rho)$, $\lambda(\tau)$, $\lambda(A)$, and $\lambda(W)$ represent the limit of error for each of the measured quantities. On a relative basis, the limit of error is

$$\frac{\lambda(\phi)}{\phi} = \frac{\lambda(\rho)}{\rho} + \frac{\lambda(\tau)}{\tau} + \frac{\lambda(A)}{A} + \frac{\lambda(W)}{W} \qquad (5)$$

i.e., the relative limit of error of the volume solids is equal to the sum of the relative limit of error for each experimentally determined quantity.

The limit of error in the density, $\lambda(\rho)$ can be taken as the limit specified in ASTM D 1475 Density of Paint, Varnish, Lacquer and Related Products since this method is used.[b] The value of the limit is 0.915 lb/gal. (0.002 kg/L) which represents 30 (u is the variance) limits. Using the density of water as 8.331b/qal as a reference point, the relative error limit is~O.2 per cent. Since most piqmented paints will have a density greater than that of water, the relative error value of 0.2 per cent is probably an upper limit.

The relative error in the weight of the wet sample is expected to be extremely small since the weight, determined to a tenth of a milligram (0.1 mg.), is on the order of 100 mg. This gives a relative error on the order of 0.1 per cent. This error, of course, may be larger depending on the volatility of the solvent blend in any particular paint. If rapid weight loss is a problem, it can be easily minimized by dispensing the wet sample from a syringe as cited in ASTM D 2369-73 Volatile Content of Paints.[6] The weight of wet paint deposited is then determined by the weight change of the syringe.

The errors associated with the area of the dish holding the wet and dry paint can be made small by using evaporating dishes which are constructed of aluminum and have smooth, flat bottom. and nearly vertical sides.[7] If the nominal 50 mm diameter is accurate to O.1 mm, the relative error becomes

$$\frac{\lambda(A)}{A} = \frac{0.2\,mm}{50\,mm} = 0.004 \qquad (6)$$

Again, one can reasonably expect a maximum error on the order of a few tenths of a per cent.

The accurate measurement of film thickness is the critical part of the proposed approach to volume solids measurements. For the factors briefly explored above, the cumulative, relative error is 1 per cent as a maximum. For a first look at the film thickness precision, one can use data supplied on rough ASTM methods of film thickness measurement. If a non-magnetic sample cup is used, an instrument based on eddy currents induced in the substrate metal can be used. From an ASTM D 1400-67 round robin testing with eddy current instruments, the standard deviation between results from different laboratories was 0.11 mil.[8] If 1.96G is taken as the limit for the error, (95 per'cent confidence limits), the limit of relative error is

$$\frac{\lambda(\tau)}{\bar{\tau}} \simeq \frac{0.22}{3} \simeq 0.072 \qquad (7)$$

using 3 roils as a typical film thickness.

It should be noted that the "in lab" standard deviation was 0.055

mil; this reduces the error limit to “4 per cent in equation (7).

Keane and Shoemaker have reported on film thickness measurements for coatings on structural steel using various magnetic gages.[9] They conclude that the instruments are inherently accurate to within 15 per cent of the true thickness and that the accuracy is improved by several thickness determinations and averaging. This can also be seen in data reported below.

Table 1 contains the analysis of film thickness measurements using two different, commercial magnetic gages. This data was supplied by W. R. Tooke, Jr.of the Micro-Metrics Company[10] In Table 1, the average film thickness, the per cent error defined as

$$\frac{\Delta\tau}{\tau} = \frac{\tau\text{measured} - \tau\text{shim}}{\tau\text{shim}} \times 100 \qquad (8)$$

and the per cent relative error limit defined as

$$\frac{\lambda(\tau)}{\bar{\tau}} = \frac{1.96\sigma}{\bar{\tau}} \times 100 \qquad (9$$

are reported. The limit of error is taken as 1.96 σ ; for a normal distribution this represents the 95 per cent confidence limit.

Table 1. Precision and Accuracy of Some Film Thickness Measurements

Instrument	Nominal Film Thickness (mil)	Average Film Thickness (mil)	$\lambda(\tau)$(mil)	$\frac{\Delta\tau}{\tau}$ (%)	$\frac{\lambda\,\tau}{\bar{\tau}}$ (%)
Zorelco[a] 747-F	3.00	3.3	0.4	10	12
	4.73	5.0	0.4	5.7	8.4
	9.77	10.2	1.6	4.4	15
Zorelco 747-NF	3.00	2.9	0.5	3.3	17
	4.73	4.7	1.3	-0.6	28
	9.77	9.7	1.5	-0.7	15
Verimeter[b]	3.00	3.4	0.3	13	8.8
	4.73	5.3	0.7	12	13
	7.70	8.2	0.4	6.5	4.9

a Zorelco Ltd., P. O. Box 4444, Cleveland, Ohio 44125; tel. 216-441-6100
b Micro-Metrics Company, P. O. Box 13804, Atlanta, Georgia 30324; tel. 404-325-3243.

In general, the accuracy is better than the precision for this set of data. It is felt that this is due to a small sample size and different calibration standards used in generating the data. The average thickness is for four measurements but these four are two sets of duplicates only with each duplicate set measured after calibration with different standards. The precision of the thickness measurements is better exemplified by the analysis presented in Table 2. The data therein are presented as:

$$\bar{\tau} \quad \pm\lambda(\tau)(\text{mil})/\lambda(\tau)/\bar{\tau}(\%)$$

Table 2. Precision of Some Film Thickness Measurements

Instrument	Panel Area 1	2	3
Minitector[a]	(6.3±0.l/2.3	16.3±0.7/4.3	1.2±0.2/17
Verimeter[b]	6.1±0.1/1.6	15.7±0.5/3.2	1.3±0.2/15

a Zormco Electronics Corporation, 8520 Garfield Blvd., Cleveland, Ohio 44125; telephone: 216-441-6100

b Micro-Metrics Company, P. O. Box 13804, Atlanta, Georgia 30324 ; telephone: 404-325-3243.

The data supplied by W. R. Tooke, Jr. of Micro-Metrics Company, was part of an ASTM round robin on dry film measurement. The average value reported is for six film thickness values measured in sets of threaon two consecutive days. The precision is much better than that reported in Table 1, reflecting a better sample size and better calibrating procedures. The higher relative error for thin film, i.e., those 1 mil, reflect the greater difficulty in determining the thickness of thin films. The absolute limit of error is still small: 0.2 mil. Since most marine coatings are used at thicknesses closer to the 6 and 16 mil figures of Table 2, it seems reasonable to use their limits of error in the total error analysis.

From the above, it is concluded that the Iimit of relative error the film thickness measurements using magnetic and eddy-current gages is on the order of 5-7 per cent. Hence, the final estimate of the limit of error for volume solids determined by accurate film thickness measurements is less than 10 per cent.

The precision or reproducibility of the present ASTM method is given as ± 1.6 per cent absolute if water was the displaced fluid and ±3.9 per cent absolute if a hydrocarbon solvent is used.[2] These are values for agreement between the average of duplicate measurements in different lab-

oratories. The relative limits depend, obviously, on the volume solids of the paint. None of the paints used in developing ASTM D 2697-73 were of the newer, high solids variety so the volume solids were most likely below 50 per cent and quite possibly below 40 per cent. On a relative basis then, the expected precision is in the range of 3-10 per cent. Hence, it appeared that the film thickness approach had merit and should be pursued in more detail. In addition, it was felt that the film thickness approach may be more convenient and rapid than the ASTM method since the measurement of film thickness is fast and eliminates errors due to various chemical and physical interactions between the film and the displacement fluid.

2.3 Plan of Action

2.3.1. Scope of Work

The volume solids of several types of coating systems used in the marine industry were to be determined using the proposed film measurement technique as well as the current ASTM method. The type of coatings to be examined were to include high build ketimine cured epoxies, amine and amine adduct cured epoxies, polyamide cured epoxies, vinyl based coatings, chlorinated rubber based coatings, alkyds, inorganic zincs, urethanes, and water-based coatings. Film drying or curing conditions used were to be appropriate to the chemistry involved in the film forming process. For example, the ketimine cured epoxies would be conditioned for seven days at standard conditions of 5015 per cent relative humidity and 2311 C. In total, the work was to extend the ASTM procedure to systems not used in its development and also allow a detailed, critical examination of the film thickness measurement approach.

The major steps in the program are presented in schematic form in

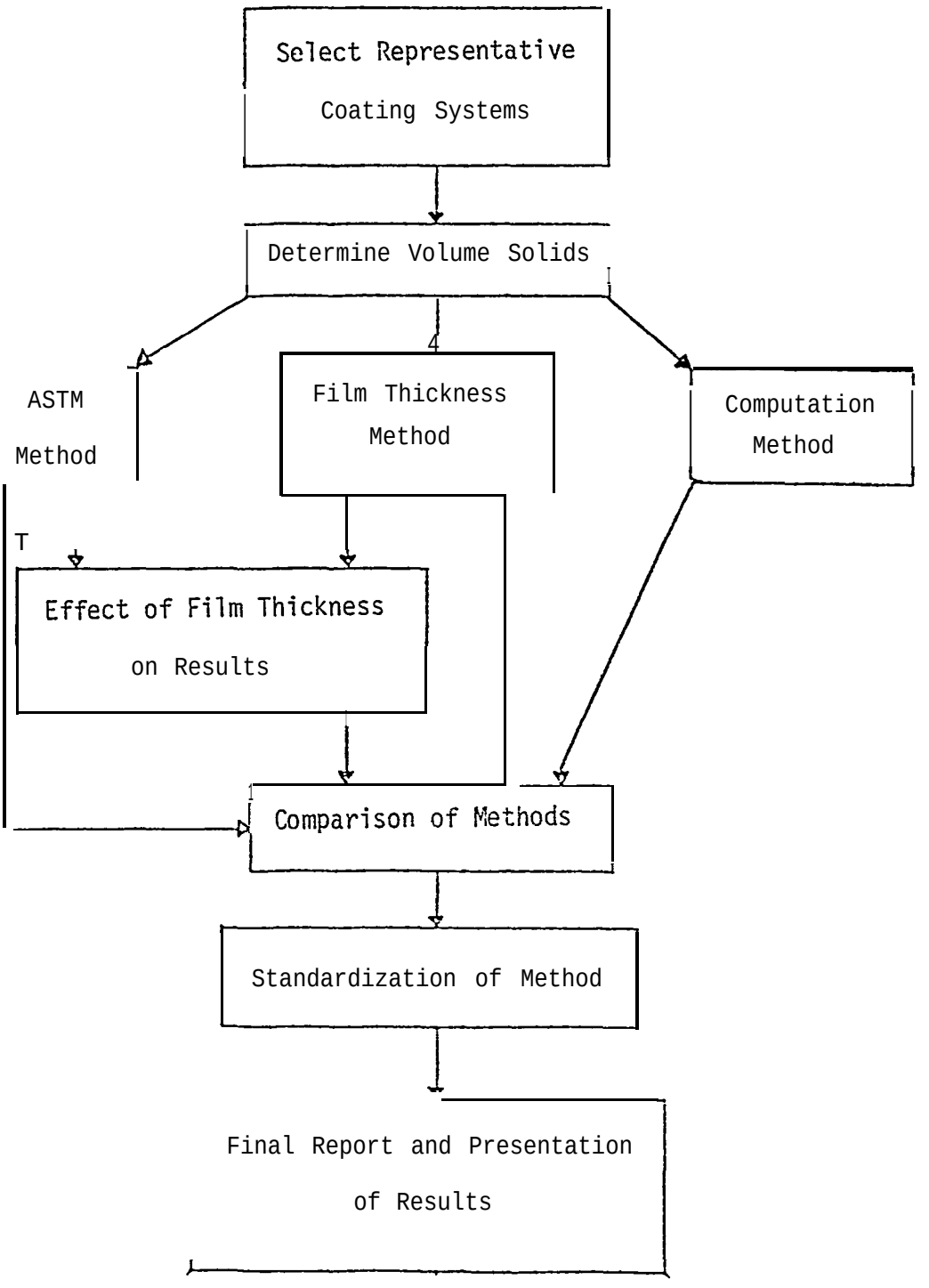

Figure 1. Schematic representation of the research plan.

Figure 1.

2.3.2. Statement of work

In order to achieve the program objectives outlined above, the tasks were:

TASK 1. Selection and Preparation of Coating Systems

The generic type of coatings to be explored in the program have been designated in 2.3.1. Scope of work.

At least two coatings of each generic type were to be selected with consultation with the Program Manager for volume solids analysis. This was done to insure that the coatings were representative of those used in the marine industry.

The selected coatings that were used in this project were commercial paint products currently being supplied to the marine industry.

TASK 2. Volume Solids Determination

Subtask 2.1 Volume Solids Determination by ASTM D-2697-73 Standard

or Pigmented Coatings.

Analyze each coating selected in Task 1 for volume solids according to ASTM D 2697-73. The values were based on at least four measurements, and characterized by standard statistical techniques (e.g. mean and standard deviation). The density of the wet paint was also determined according to ASTM D 1475-50 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. The films were dried or conditioned with respect to the appropriate chemistry of the materials and as close to field use conditions as practicable. The approximate film thickness or weight was representative of field use thickness, as recommended by the paint manufacturer. The effect of forced drying/curing on the volume

solids value was also explored using the procedure in ASTM D 2697-73.

Subtask 2.2 Volume Solids Determination by Precision Film Thickness Measurement.

Each of the coatings selected in Task 1 was analyzed for volume solids by the method outlined in section 2.2.1. That is, the volume solids determination was derived from an indirect measurement of wet volume and a direct measurement of dry film thickness and volume. For the paints under study, the density determined in Subtask 2.1 was used to calculate the wet volume of the paint. The procedure followed is given below.

Two film thickness measurement instruments were used. One is a dial guage micrometer as outlined in ASTM D 1005; the other instrument is an eddy current device.[11] These were used to measure the bottom thickness of the evaporating dishes. The thickness was determined by averaging readings from ten different spots in each dish. The approximate amount of paint was deposited into the dishes to give the desired final film thickness; efforts were made to spread the paint uniformity over the bottom of the dish by spinning at low speed. The paint was then allowed to dry or cure as appropriate. At the end of the curing schedule, the film thickness of the dry coating was measured with the two film measuring instruments with the measurements being made at the same positions in the dish without paint. The volume solids were then calculated based in the film thickness, area of the dish, wet paint density, and wet paint weight. Four determinations were made for each paint. The set of values were characterized by standard statistical techniques.

Subtask 2.3 Effect of Film Thickness on Volume Solids Values

The effect of film thickness on the volume solids values obtained was explored by determining the volume solids at two thickness levels,

one greater than typically used and one less than typically used. This was done for one coating system from each generic type. The volume solids were measured by both the ASTM method and the film thickness method, as outlined in Subtasks 2.1 and 2.2. This task was undertaken since the film structure (pores, voids, trapped solvent) obtained can be dependent of the wet film thickness. This step was also necessary to equate the volume solids of the wet, deposited films in the laboratory to the realistic values of volume solids of the wet, deposited films spray applied in a shipyard.

Subtask 2.4. Calculated Volume Solids

The selected list of coatings from Task 1 all had the manufacturer's stated volume solids on their data sheets. These values were used as the calculated volume solids.

Task 3. Comparison of Methods

The volume solids data generated in Task 2 were compared and analyzed to assess the merits of the film thickness technique against the present ASTM method. The comparison was done by determining if the differences observed in volume solids were due to experimental error. The "student's t-test" was used.[12]

The t-test statistic was calculated by the expression

$$t_{\bar{d}} = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{S_{\bar{d}}}} \quad \text{with } (n_1 + n_2 - 2) \text{ degrees of freedom,}$$

where $\bar{x}_1$, $\bar{x}_2$ represent sample means, $S_{\bar{d}}$ = the pooled sample variance, and n_1 and n_2 are the sample sizes.

The probability associated with t was obtained from tables. The level of significance used for the comparisons was 0.05.

Task 4.- Standardization of Volume Solids Measurement

In order to initiate standardization of the better method (Task 3) for determining volume solids in the marine industry, especially for coating suppliers, the results of the work, if warranted were to be presented to appropriate ASTM committees, such as F-25 Standards for Ship Building, DO1.21.24 Volatile Content of Paint, and D-1.23.12 Film Thickness (dry), submitted for publication to the Journal of Coatings Technology, and presented at a Marine Coatings Conference. However, time and budget restraints have precluded this task.

2.4 Results

Each of the coatings selected in Task 1 were analyzed for volume solids by the ASTM D 2697-73 Method. Densities of the wet coatings were measured according to ASTM D 1475-60. Table 3 summarizes the volume solid values obtained. The values reported represent the average of at least four determinations.

The volume solids of the coatings selected in Task 1 were also determined by the film thickness technique as outlined in Section 2.2.1. The values are reported in Table 4. A sample calculation is given in Figure 2.

The effect of film thickness on the volume solids values was investigated by determining the volume solids at two additional thickness levels: one greater than recommended by the manufacturer and one less than recommended. Table 4 also contains the volume solids values for these samples.

Volume solids were also determined at different curing or conditioning schedules following the basic ASTM D 2697-73 procedure. Here, the temperature was varied. The results are listed in Table 5.

2.4.1 Discussion of the volume solids results obtained by using the ASTM

Coating: Sigma-Nucol CRHB-7311 (Chlorinated Rubber)

Procedure: Wet coating placed in drying pans and weight of wet paint determined. Coating spread over bottom of the pan then allowed to dry according to manufacturer's recommended conditions. Film thickness of dried film measured at eight locations distributed over the pan bottom using either an eddy current instrument or a dial gauge micrometer.

Drying Pan Area (A): 26.42 cm^2

Density of wet coating (P): 1.3987 grams/cm^3

Weight of Wet Coating (W)

	A			
(4 samples):	1. 9798g	1.3364g	1.3508g	1. 2709g
Average Dry Film Thickness (T)	9.73 mil 0.0247cm	6.98mil 0.0177cm	6.81 mil 0.0173cm	6.38 mil 0.0162cm
Volume Solids = $(A\tau\rho)/W$				
Calculated Volume Solids (%):	46.1	48.9	47.3	47.1

Figure 2. Example Volume Solids Determination by Film Thickness Method.

D 2697-73 method.

From Table 3, the volume solids value obtained using the ASTM D 2697-73 Method was larger than the manufacturer's value except the two ketimine-cured epoxies and one alkyd coating SIGMA-7240-7000. The experimental and reported volume solid values agreed for one coating, inorganic zinc-rich Matcote 1-289.

The method used by the various manufacturers to determine volume solids values is not known. However, it is surmised that the ASTM method was not the method used because of the very high percentage of differing results.

It is also noted from Table 3 that the volume solids values obtained using the manufacturer's recommended curing schedule are also larger than the manufacturer's stated volume solids values. Exceptions are, again, the two ketimine-cured epoxies, the alkyd coating Sigma-7240-7000, and an inorganic zinc-rich coating Matcote 1-289, where the values were the same.

For the standard ASTM Method, the precision of the method is good. In most cases, the magnitude of the 95 per cent confidence band (kl.96s) is less than one per cent absolute. However, there are cases when the precision is less. These are: Farboil #99PR (ketimine cured epoxy) with volume solids of 76.3 ± 2.2 per cent; Intertuf x8921/XV 1531 (waterborne) with volume solids of 54.9 ± 2.9 per cent; Matcote 1-289 (inorganic zinc-rich) with volume solids of 63 .9 ± 2.9 per cent; Sigma MCF-7551 (inorganic zinc-rich) with volume solids of 74.7 ± 17.5 per cent. It is not known if these exceptions are indicative of specific problems in the applicability of the ASTM method to these materials or if additional experimentation would reduce the variance.

2.4.2 Discussion of the Volume Solids Results Obtained by Using the Film Thickness Measurement Method.

From Table 4, it is seen that the volume solids values determined at the manufacturer's recommended curing time (MRCT) and recommended film thickness (MRFT), are higher than the stated volume solids (MSVS) values in six of the seventeen cases and lower than the MSVS in nine cases.

In that portion of the study in which the film thickness was varied, it was found that lower film thicknesses than recommended gave lower volume solids values than those at the recommended thickness. For volume solids values determined at film thicknesses above the recommended thickness, values were higher than those obtained at MRFT. This indicates that in using the film thickness method, the possibility of trapping solvent or volatile material in heavier films could result in erroneous values.

2.4.3 Discussion of the Volume solids Values based on Results Obtained by Alterimg the Curing Temperatures in ASTM D 2697-73.

As is shown in Table 5, the volume solids values obtained under the standard curing schedule, (3 Hrs. @ 105°C) are all larger than the MSVS in seven separate types of coatings. The volume solids values obtained using the MRCT are also larger than the MSVS. In six of the seven cases, the standard curing schedule temperature is lower than the MRCT. It is also shown in Table 5 that lower curing temperatures give higher volume solids values and higher temperatures give lower volume solids values. This trend was true even for conditioning to a constant weight at a given temperature.

2.4.4 Comparison of the ASTM D 2697-73 Method and the Film Thickness Method for Obtaining Volume Solids.

The results of the comparison between the ASTM method and the film thickness method for volume solids determination are presented in Table 6.

The comparison was made based on Student's t-test to quantitatively determine if the differences observed were due to experimental errors or not. In fifteen of the twenty-one paired comparisons, the disagreement in volume solids values could not be assigned to experimental or sampling error. Hence, the two methods do not, in general, give equivalent results.

The statistics indicate that the precision of the film thickness method is much less than the precision of the ASTM method. This lack of precision is primarily due to not Seing able to obtain a uniformly thick film. Inherent in the film thickness method is a requirement for constant film thickness.

During the course of the work on this project, several methods were tried to achieve uniform film thickness:

1. It was attempted to spread the wet paint uniformly over the bottom of the dishes by spinning them at various speeds. The apparatus used is depicted in Figure 3.

The spinning apparatus was made from a small laboratory stirrer. An aluminum dish was cemented to the shaft of the stirrer. This dish served as a holder for the dishes containing the wet Paint samples. A rheostat was connected to the stirrer in order to provide variable rotation speeds.

2. The aluminum dishes were also rotated very slowly manually and placed on a level surface to cure.

3. The viscosity of the paint was lowereci with appropriate solvent and methods 1 and 2 above tried.

4. Aluminum dishes containing wet Paint were placed in an ultrasonic bath containing water to allow the vibrations to produce a uniform film.

5. Method 4 was also attempted using liquids denser than water, e.g., trichloro-trifluoroethane and methylene chloride. Liquids lighter than water were also used, e.g., mineral spirits and VM & P naphtha.

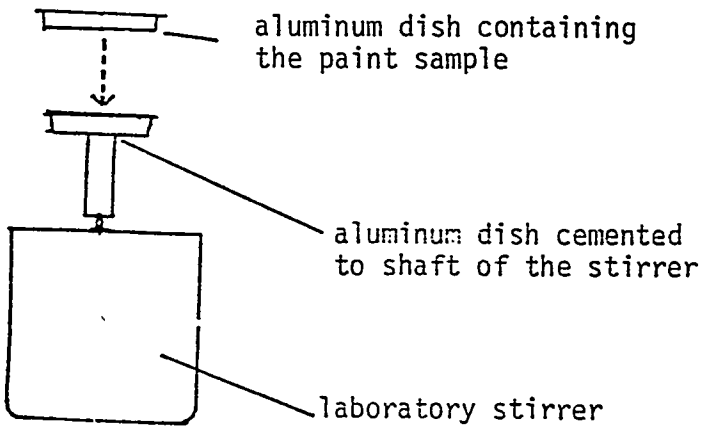

Figure 3. Diagram of spinning apparatus

All of the above methods failed to consistently produce sufficiently uniform film thicknesses to give the film thickness method the precision of the ASTM method.

Lastly, under equivalent curing or conditioning schedules, there was no savings of time or sample handling with the film thickness method over the ASTM method. In fact, in many instances, the time was actually longer.

TABLE 3

VOLUME SOLIDS AS DETERMINED BY

THE ASTM D 2697-73 STANDARD METHOD

PAINT	*MSVS	ASTM D 2697-73 3 hrs @ 105°C	**MRCT
I. High-Build Ketimine Cured Epoxy			
1. Farboil #99	87.0	73.5	76.7
2. Farboil #99 PR	87.0	76.3	85.0
II. Amine and Amine Adduct Cured Epoxy			
1. Carboline - 187HFP	66. 0±l	68.6	73.8
2. Napko - 7-2371	44.3	55.6	57.8
3. Sigma - EHB - 7433	70.0	76.6	80.8
III. Polyamide Cured Epoxy			
1. Deco-Rez-DE-3490	40.0	44.3	45.2
2. Matcote Co. - 1-844	50.C±2	63.7	67.2
3. Carboline - 193	50.c±l	56.4	57.3
IV. Vinyl Coatings			
C-Flex Imperial Co.-#32l	28.0±l	42.4	46.3
2. Sigma-NUCOL #7352	24.0	24.2	26.1
\/. Chlorinated Rubber			
1. Carboline-3631HB	34.±l	39.3	44.9
2. Sigma NUCOL-7311	47.o±l	49.9	52.6
VI. Urethanes			
1 carboline - 132	55.c±l	56.3	55.8
2. Imperial--#1001	46.0	54.3	56.6
VII. Mater-base Coatings			
1. International Intertuf-X8921/XV1531	53.5	55.9	53.8
2. Sigma-7445	39.0	52.9	53.6
3. Porter-Epoxy 6610	36.4±2	41.7	42.7

*Msvs - Manufacturer's Stated Volume Solids
**MRCT - Manufacturer's Recommended Curing Time

TABLE 3

VOLUME SOLIDS AS DETERMINED BY

THE ASTM D 2697-73 STANDARD METHOD (Cont'd)

PAINT	*MSVS	ASTM D 2697-73 3 hrs @ 105°C	**MRCT
VIII. Alkyd Coatings			
1. Matecote-2400	35.0±2	44.7	46.3
2. Sigma - 7240-7000	50.0	41.0	44.1
IX. Inorganic Zinc-rich Coatings			
1. Matcote 1-289	63.9	63.9	63.9
2. Sigma MCF-7551	56.0	74.7	74.2

*MSvs - Manufacturer's Stated Volume Solids
**MRCT - Manufacturer's Recommended Curing Time

TABLE 4

VOLUME SOLIDS DETERMINED BY THE FILM THICKNESS MEASUREMENT METHOD

Coatings	*MSVS	**MRFT	L	L-GAGE MICRO		ILR		****		"AL-SCOPE" MO		L AE	
			VOLUME SOLIDS	***D.F.T. MRFT	VOLUME SOLIDS	D.F.T below MRFT	VOLUME SOLIDS	D.F.T. above MRFT	OLUME OLIDS	*** D.F.T. MRFT	VOLUME SOLIDS	D.F.T below MRFT	VOLUME OLIDS	D.F.T. above MRFT
I. High-Build Ketimine-Cured Epoxy														
1. Farboil #99E	87.0	4-6	61.1	6.2	65.6	3.3	59.5	7.1			68.4	3.5		
2. Farboil #99 PR	87.0	4-6	67.4	4.8			66.7	6.5	67.0	4.8			68.4	7.6
II. Amine and Amine Adduct Cured Epoxy														
1. Carboline-187 HFP	66.0	4-8	78.1	7.6			78.8	8.4						
2. NAPKO-7-2371	44.3	2-4	43.3	3.0	40.9	1.9	45.6	4.1	41.6	2.9	40.1	1.9	43.2	3.9
3. SIGMA - EHB-7433	70.0	10.0	75.8	10.2	67.3	5.6	82.0	13.9			65.1	5.3		
III. Polyamide Cured Epoxy														
1. Deco-Rez-DE-3490	40.0	2-5	40.0	3.6	28.1	2.0	46.0	6.8	41.2	3.6	31.7	2.0		
2. Matcote Co.-1-844	50.0	2-3					57.1	3.4						
3. Carboline-193	50.0	3-4	56.4	3.2			66.5	4.1						
IV. Vinyl Coatings														
1. Imperial - C-Flex #321	28.0	3-4	59.8	3.5	28.6	1.6	57.6	5.4	63.0	3.6	48.4	1.5	58.7	4.4
2. SIGMA-NUCOL #7352	24.0	3.0	24.2	3.3	21.0	2.3	26.2	3.9	28.3	3.8	23.2	2.4	29.3	4.4
V. Chlorinated Rubber														
1. Carboline-3631HB	34.0	3-0			22.0	2.3								
2. SIGMA-NUCOL - 7311	47.0	3-4	44.5	3.8	44.8	2.2	48.6	6.6	47.8	3.9	45.6	2.4	50.4	6.6
VI. Urethanes														
1. Carboline-132	55.0	1.5-2.(	44.8	1.9			45.8	2.3						
2. Imperial-#1001	46.0	2-3	45.8	2.5	36.7	1.4	48.1	4.4	52.5	2.9	38.1	1.4	46.1	4.2

* MSVS - Manufacturer's stated volume solids (%)
** MRFT - Manufacturer's recommended film thickness (Mils)
*** D.F.T. MRFT-Dry film thickness in the manufacturers recommended film thickness range (Mils)
**** Eddy - Current film thickness measuring instrument-(Maximum thickness Measurements-8 Mils)

TABLE 4

VOLUME SOLIDS DETERMINED BY THE FILM THICKNESS MEASUREMENT METHOD (Cont'd)

Coatings	*MSVS	**MRFT	DI	-GUAGE MICROM	ER		****"D	L-SCOPE" MO	L At	
			VOLUME SOLIDS	*** D.F.T. MRFT	VOLUME SOLIDS	D.F.T. below MRFT	VOLUME SOLIDS	D.F.T. above MRFT	VOLUME SOLIDS	*** D.F.T. MRFT	VOLUME SOLIDS	D.F.T. below MRFT	VOLUME SOLIDS	D.F.T. above MRFT
VII. Water-based Coatings														
1. International-Intertuf X8921/XV1531	53.5	7-14	48.9	9.5	45.4	5.6					53.1	6.5		
2. Sigma-7445	39.0	3.2	51.2	3.3	50.0	2.4	54.3	4.6	46.8	3.3	47.0	2.2	51.8	4.5
3. Porter-Aqualock-6610	36.4	2.5	34.6	2.6	32.3	1.8	34.6	5.0	33.1	2.6	30.8	1.9	34.0	3.6
VIII. ALKYD COATINGS														
1. Matecote Alkyd-2-400	35.0	1.5	28.7	1.6	25.1	1.4	33.6	1.8						
2. Sigma-7240-7000	50.0	1.5	25.6	1.5	24.5	1.4	30.1	2.6	24.0	1.6	25.3	1.4	33.5	2.9
IX. Inorganic Zinc-rich Coatings														
1. Matecote - 1-289	63.9	3-5					70.5	5.9						
2. Sigma-MCF-7551F	56.0	2.0					74.5	3.9						

* MSVS - Manufacturer's stated volume solids (%)
** MRFT - Manufacturer's recommended film thickness (Mils)
*** D.F.T. MRFT-Dry film thickness in the manufacturers recommended film thickness range (Mils)
**** Eddy - current film thickness measuring instrument-(Maximum thickness Measurements-8 Mils)

TABLE 5

COMPARISON OF VOLUME SOLIDS RESULTS
BY ALTERING THE ASTM D 2697-73 METHOD
CURING TEMPERATURES

PAINT	MSVS*	MRCT**	CT-VS**	VOLUME OLIDS T STATED TEMPER URES				
				Hrs. @ 21°F 05°C	*** 50°F 5.5°C	*** 00°F 3.3°C	**** 248°F 20°C	*** 03°F 50°C
CHLORINATED RUBBER								
Carboline-3631 HB	4±1	5 Hrs. 75°F (24°C)	4.9	39.3	40.1	38.1		
Sigma-NUCOL 7311	7±1	8 Hrs. 68°F (20°C)	2.6	49.9		53.5		
URETHANE								
Carboline 132	±1	5 days 90°F (32°C)	5.8	56.3	53.1	48.8		
AMINE ADDUCT CURED EPOX								
Napko 7-2371	4.3	2 days 75°F (24°C)	47.8	55.6			49.9	46.0
AMINE CURED EPOXY								
Carboline-187 HFP	5±1	20 Hrs. 150°F (66°C)	73.8	68.6	71.7	70.7		
POLYAMIDE CURED EPOXY								
Deco-Rez-DE-3490	0.0	12-14 H 77°F (25°C)	45.2	44.3			38.5	38.1
Matcote 1-844	0±2	18 Hrs 77°F (25°C)	67.2	63.7	61.4	60.5		

*MSVS-Manufacturer's Stated Volume Solids
**MRCT-Manufacturer's recommended Curing Temperature
***MRCT-VS-Manufacturer's Recommended Curing Temperature-Volume Solids
**** - Samples heated until constant weight obtained.

TABLE 6

Student's t-Test of Statistical Significance Between ASTM D 2697-73 and Film Thickness Method

PAINT	$\bar{X}_1 \pm 1.965$ ASTM Method V.S. Sample Means	$\bar{X}_2 \pm 1.965$ F.T.M. V.S. Sample Means	n_1 Sample Size ASTM Method	n_2 Sample Size F.T.M.	S_1^2 Variance ASTM Method	S_2^2 Variance F.T.M.	S^2 Pooled Estimate Variance	$S_{\bar{d}}$ Sample Variance for Diff. in sample means	$t_{\bar{d}}$ Comparison of Means	Pr(t) Probability/ t	CONCLUSION
KETIMINE CURED EPOXY											
1. Farboil #99E	73.5±2	61.1± 9.8	4	4	.010	25.06	25.06	2.50	4.96	.002	Difference Due to Method
2. Farboil #99PR	76.3±2.2	66.7± 28.6	4	4	1.300	212.20	106.75	7.31	1.32	.241	Sampling Difference
AMINE & AMINE ADDUCT CURED EPOXY											
3. Carboline 137HFP	68.6±2	78.1±2	4	2	.016	1.05	.27	.45	21.16	.000	Difference Due to Method
4. NAPKO 7-2371	55.6±.4	43.3 ± 5.6	4	4	.046	8.19	4.12	1.44	8.57	.000	Difference Due to Method
5. Sigma EHB-7433	76.6±3	75.8 ± 6.7	4	4	.017	45.51	22.76	3.37	.24	.848	Sampling Difference
POLYAMIDE CURED EPOXY											
6. Deco-Rez-DE-3490	44.3±.1	40.0±5	4	4	.003	25.61	12.81	2.53	2.06	.086	Sampling Difference
7. Matcote Co.-1-844	63.7±.2	57.1±3	4	3	.011	8.86	3.55	1.44	4.58	.004	Difference Due to Method
8. Carboline-193	56.4±.5	56.4 ± 6.7	4	2	.065	11.80	3.00	1.20	0.00	1.000	Sampling Difference
VINYL COATINGS											
9. Imperial Co. G-Flex	42.4±.37	28.6 ± 2.7	4	3	.035	1.88	1.16	.82	16.80	.000	Difference Due to Method
10. Sigma-NUCOL #7352	24.2±.26	23±4.8	4	3	.018	1.96	2.39	1.18	3.81	.009	Difference Due to Method
CHLORINATED RUBBER											
11. Carboline 3631HB	39.3±.36	21.3 ± 4.4	4	4	.033	5.15	2.59	1.14	15.82	.000	Difference Due to Method
12. Sigma NUCOL-/311	49.9±.09	47.4 ± 2.4	4	4	.002	1.44	.96	.69	3.61	.011	Difference Due to Method

* V.S. - Volume Solids
** F.T.M. - Film Thickness Method

TABLE 6 (Continued)

Student's t-Test of Statistical Significance Between
ASTM D 2697-73 and Film Thickness Method

PAINT	$\bar{X}_1 \pm 1.96s$ ASTM Method Volume Solids Sample Means	$\bar{X}_2 \pm 1.96s$ F.T.M. Volume Solids	n_1 Sample Size ASTM Method	n_2 Sample Size F.T.M.	S_1^2 Variance ASTM Method	S_2^2 Variance F.T.M.	S^2 Pooled Estimate Variance	$S_{\bar{d}}$ Sample Variance for Diff. in sample	$t_{\bar{d}}$ Comparison of Means	PR(t) Probability/ t	CONCLUSION
URETHANES											
13. Carboline-132	56.3±.5	51.5 ± 6.6	4	3	.073	11.21	4.53	1.63	2.95	.024	Difference Due to Method
14. Imperial-#1001	54.3±.2	47.0 ± 9.1	4	4	.013	21.67	10.84	2.32	6.29	.000	Difference Due to Method
WATER-BASE COATINGS											
15. International Intertuf X8921/XV1531	54.9±2.9	48.9 ± 2.8	4	4	2.168	2.09	2.13	1.03	5.83	.000	Difference Due to Method
16. Sigma-7445	52.9±3.9	50.4 ± 7.6	4	4	3.953	14.93	9.44	2.17	1.52	.184	Sampling Difference
17. Porter Epoxy 6610	41.7±37	34.2 ± 2.6	4	4	.036	1.70	.87	.66	11.38	.000	Difference Due to Method
ALKYD COATINGS											
18. Matecote-2400	44.7±.3	33.6 ± 5.3	4	3	.035	7.29	2.94	1.31	8.49	.000	Difference Due to Method
19. Sigma-7240-7000	41.0±.2	33.1 ± 6.6	4	3	.015	11.33	4.54	1.63	10.61	.000	Difference Due to Method
INORGANIC ZINC-RICH COATINGS											
20. Matecote 1-289	63.0±.9	70.5± 8.7	4	3	2.130	19.77	9.19	2.32	2.84	.036	Difference Due to Method
21. Sigma MCF-7551	74.7±17.5	74.5± 11.3	4	2	79.710	33.06	96.24	8.50	.02	1.000	Sampling Difference

* F.T.M. - Film Thickness Method

SECTION 3
Bibliography

3. BIBLIOGRAPHY

1. Ginsberg, Thomas, "Measurement of the Film Build Ability of Paints," Materials Performance 15, (2), 21-25 (1976).

2. 1976 Annual Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia, 1976, pp. 526-528.

3. Conversation of Frank A. Rideout (Georgia Tech) with Mr. A. S. Abbott, Chairman ASTM DO1-21.24.

4. Shoemaker, D. P. and Garland, C. W., Experiments in Physical ChemistrY, McGraw-Hill Book Company, New York, 1962,pp. 30-35.

5. 1976 Annual Book of ASTM Standards, Part 27, American Society for Testing and materials, Philadelphia, 1976, pp. 238-240.

6. 1976 Annual Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia, 1976, pp. 447-448.

7. 1979 Catalogue, Fischer Scientific Company, stock number 8-7325C, p. 253.

8. 1976 Annual Book of ASTM Standards, Part 27, American Society for Testing and Materials, Philadelphia, 1976, pp. 226-230.

9. Keane, J. D., and Shoemaker, T. L., "Development of Specifications for Measurement of Paint Thickness on Structural Steel," J. Paint Technology 45 (585), 46-67 (1973).

10. Tooke, W. R. Jr., Micro-Metrics Company, P. O. Box 17804, Atlanta, Georgia 30324; telephone 404/325-3243.

11. Twin-City Testing Corporation, North Tonawanda, New York, Dual Scope

12. Nie, N. H.; Hull, C. H.; Jenkins, J. G.; Steinbrenner, K.; and Bent, D. H., Statistical Package for the Social Sciences; Mcgraw-Hill Book Company, New York, 1975, pp. 267-269.

13. Meyer, Stuart L., Data Analysis for Scientists and Engineers, John liiley & Sons, Inc., New y ork, 1975, pp. 279-281.

SHIP PRODUC
FACILITIES IN
OUTFITTING AND
INDUSTRIAL ENGINEERING
SHIPBUILDING S
DESIGN/PRODUCT
COMPUTR AIDS F
SURFACE **PREPARATION**
ENVIRONMEI
TECHNOL
W
R